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Structures of 6H-SiC Surfaces

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Abstract. We have systematically studied reconstructions of the 6H SiC(0001) and (000 $\bar{1}$) surface under both Si rich and C rich condition using field ion-scanning tunneling microscopy (FI-STM). The sample was cleaned by in situ Si beam etching at 900-1000 °C. The Si rich and C rich phases were produced by annealing the sample in a Si flux and C₂H₂, respectively. On the (0001) surface, the as-cleaned surface showed ($\sqrt{3}\times\sqrt{3}$) reconstruction. With increasing Si concentration, (2x2), (2 $\sqrt{3}\times 6\sqrt{3}$), (3x3), and (7x7) reconstructions were observed. Reaction of the Si rich phases with C₂H₂ molecule at 1050 °C resulted in the formation of C rich surface, which exhibited (2x2)/(6x6) reconstruction. On the (000 $\bar{1}$) surface, (2 $\sqrt{3}\times 2\sqrt{3}$) reconstruction was observed after cleaning. Under Si rich condition, (2x2), (3x3), and (7x7) reconstructions were observed. Annealing the surface in C₂H₂ beam at 1050 °C led to C rich phase with (1x1) structure. Structure model for ($\sqrt{3}\times\sqrt{3}$) and (2 $\sqrt{3}\times 2\sqrt{3}$) reconstruction are proposed, and possible applications of using the surface reconstruction to selectively grow the polytype SiC is discussed.

1. INTRODUCTION

Silicon carbide (SiC) is a wide band gap semiconductor with potential applications for short wavelength optoelectronic, high temperature, radiation resistant, and high-power electronic devices. SiC crystallizes in either a cubic or a hexagonal form, and exhibits polytypism which is derived from different stacking sequences of Si/C bilayers along the closest packed direction. The lone cubic, zinc-blende form of SiC is referred to as β -SiC whereas the numerous polytypes of the hexagonal and rhombohedral forms are collectively referred to as α -SiC, among which 4H and 6H are the most common. Despite identical stoichiometry, SiC polytypes differ in their electronic energy band gap by as much as 1 eV. This opens up interesting perspectives for the development of multi-layer structure such as 4H/6H/4H/6H ..., etc. which is a new material with controllable band gap. Unfortunately, the growth process of SiC layers with predesigned polytypes has yet to be achieved in a controlled manner. Chemical vapor deposition (CVD) is the primary route for homoepitaxial growth of 6H and 4H films at temperature above 1200 °C [1]. Molecular beam epitaxy (MBE) has been used to lower the growth temperature [2,3]. Epitaxial growth of 6H-SiC films on the vicinal 6H-SiC(0001)-(3x3) surface was achieved by gas source MBE at 1050 °C [3]. The reduction of growth temperature was attributed to the enhanced adatom mobility on the (3x3) surface. A very recently study suggested that atomic layer epitaxy (ALE) is a likely way to achieve the growth of definite SiC polytypes [4]. Therefore, detailed analysis of the atomic structure of the 6H-SiC surface is needed to clarify the conditions necessary to obtain a specific polytype of SiC.

2. EXPERIMENTAL

The experiments were carried out in a UHV chamber containing a scanning tunneling microscopy (STM) equipped with a low energy electron diffraction (LEED) and a field-ion microscope (FIM) which was used to monitor and fabricate the STM tip. Details of the FI-STM experimental set-up have been discussed elsewhere [5]. Samples were n-type ($n=2\times 10^{18}$ cm⁻³) 6H-SiC single crystals supplied by Cree Research. The surface was cleaned in situ by Si molecule beam etching at 900-1000 °C. The temperature was

measured using an optical pyrometer with an emissivity setting of 0.53. The Si beam was produced by heating a small Si slab to 1100-1150 °C positioned at 10 cm away from the sample. The Si flux was estimated to be in the range of 10^{14} to 10^{15} $\text{cm}^{-2}\text{s}^{-1}$. Carbon source was acetylene (C_2H_2), and it was leaked into the chamber through a leaking valve. All STM images were taken with sample bias -2.0 V, unless specified.

3. RESULTS AND DISCUSSION

3.1 Structures of the Si-terminated surface

After exposing the SiC(0001) surface to Si flux at 950 °C for 5 minutes, the surface was clean and exhibited large terraces of up to 500 Å. The majority of the steps had height of about 7 Å, which was close to three bilayers high (7.6 Å). On the terraces, high resolution dual bias images (Fig. 1(a)&(b)) showed a honeycomb structure in the filled-state (a) and a hexagonal structure in (b) the empty-state with height contrast reversal. The measured unit cell spacing was 5.4 ± 0.2 Å, in good agreement with the expected value of 5.3 Å for the $(\sqrt{3}\times\sqrt{3})$ reconstruction, and the corrugation was typically 0.2 Å. This structure has been reported in previous studies [6,7,8], and a Si adatom on the T_4 site has been suggested. A recent first-principles total-energy calculations also supported the Si- T_4 adatom model, and the calculated electronic structure showed a metallic and half-filled surface state, which suggested that the STM images were similar for tunneling in and out of the surface [9]. However our STM result shown in Fig. 1(a)&(b) was inconsistent with the T_4 adatom model since the STM images in the filled-state and empty-state showed a height contrast reversal. This Si- T_4 model was also inconsistent with recent photoemission study [10] which showed a semiconducting surface state with for the $(\sqrt{3}\times\sqrt{3})$ structure.

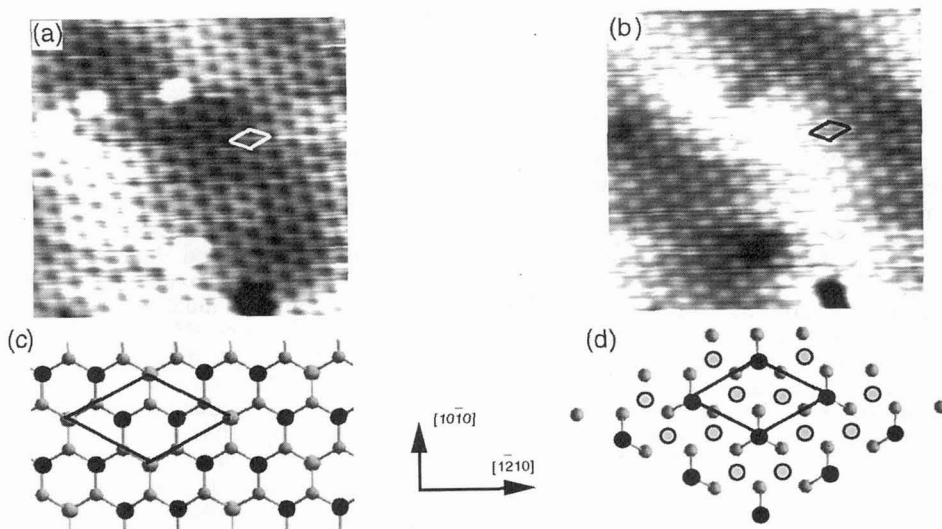


Figure 1: (a) Filled-state (-1.2 V), and (b) empty-state (+1.2 V) image of the $(\sqrt{3}\times\sqrt{3})$ reconstruction ($70\text{\AA}\times 70\text{\AA}$). (c) Top view of the surface vacancy model. Large and small ball is the Si and C atom of the Si/C bilayer respectively, and dark ball is the C adatom. (d) Top view of the Si-C alloy model. The top layer Si is shown in dark ball, and the C that substitutes Si is shown in grey.

Based on our STM results, a surface vacancy model for this $(\sqrt{3}\times\sqrt{3})$ structure was proposed [11]. Referring to Fig.1 (c)&(d), which show the surface vacancy model and another possible surface Si-C alloy model for the $(\sqrt{3}\times\sqrt{3})$ reconstruction. In the surface vacancy model, a complete layer of C adatom adsorbed on the outer Si-C bilayer with one third of its adatom missing creates the vacancy which produces the $(\sqrt{3}\times\sqrt{3})$ geometry. The C adatoms reside on the atop sites, and the dangling bond of the Si

atom at the center of the vacancy is unsaturated. In the surface Si-C alloy model, $2/3$ of the surface Si atoms is substituted by C atoms in a manner that creates the $(\sqrt{3}\times\sqrt{3})$ geometry. In both models, we assume $2/3$ of ML of Carbon on the surface although the crystallographic orientation for the surface is Si-terminated. The fact that this $(\sqrt{3}\times\sqrt{3})$ is formed at about 1000°C suggests that Si depletion on the surface could happen. Also previous XPS and AES studies have indicated that carbon segregation can occur at temperatures as low as 900 K [12]. Simple electronegativity considerations indicates that charge transfer is mainly from Si to C. As a result of the charge transferring, it can be expected that C atoms are likely to be revealed in filled-state STM image, and Si atoms to be revealed in empty-state STM image. Thus, the surface Si-C alloy model is preferred. However, we should note that the relation between STM images and the surface geometric structure is complicated. Our proposed models for the $(\sqrt{3}\times\sqrt{3})$ structure are therefore tentative, and further studies are needed.

When the $(\sqrt{3}\times\sqrt{3})$ surface was exposed to the Si beam, four more distinctive surface phases have been found as shown in Fig. 2(a) to (d) as a function of increasing Si concentration. The first phase formed is shown in Fig. 2(a), after deposition of Si on the $(\sqrt{3}\times\sqrt{3})$ surface at 850°C for about 1 minute. The surface showed local (2×2) ordering. Figure 2(b) shows the surface after further deposition of Si on the (2×2) surface, and the structure was determined to be $(2\sqrt{3}\times 6\sqrt{3})$ reconstruction. The atomic arrangement of the $(2\sqrt{3}\times 6\sqrt{3})$ structure can be seen to form two types of rows, one type containing four maxima and the other containing two maxima. Deposition of more Si on the $(2\sqrt{3}\times 6\sqrt{3})$ produced a hexagonal array of protrusions with corrugation of 2.5 \AA that formed the (3×3) reconstruction (Fig. 2(c)). It is apparent that the our STM images of the (3×3) reconstruction is once again inconsistent with the model proposed based on the Si(111)- (7×7) dimer-adatom-stacking fault (DAS) model in the previous LEED and ELS studies [6], since the very prominent corner holes of the DAS (3×3) structure are absent in both filled-state and empty-state STM images. Eventually, the (7×7) DAS structure was produced by deposition of Si on the (3×3) surface (Fig. 2(d)). Accompanying the (7×7) reconstruction, the step structure also changed from relative straight when surface was $(\sqrt{3}\times\sqrt{3})$ reconstructed to be triangular shaped, and the step edge was oriented along $\langle 1120 \rangle$ directions. The change of surface morphology was likely resulted from the large lattice mismatch between Si and SiC (20% for Si and β -SiC). Annealing the surface at around 1000°C resulted in Si desorption, which led to successive transformation of those phases.

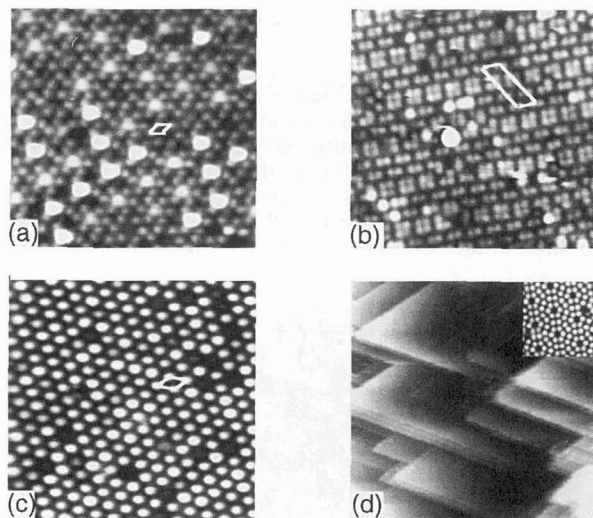


Figure 2: Sequence of STM images of the 6H-SiC(0001) surface, showing the Si rich structures in the order of increasing Si concentration: (a) The (2×2) reconstruction ($120\text{ \AA}\times 120\text{ \AA}$); (b) The $(2\sqrt{3}\times 6\sqrt{3})$ reconstruction ($118\text{ \AA}\times 118\text{ \AA}$); (c) The (3×3) reconstruction ($160\text{ \AA}\times 160\text{ \AA}$); (d) The (7×7) reconstruction ($1200\text{ \AA}\times 1200\text{ \AA}$). The insert shows an empty-state image (+2V) of the (7×7) structure.

The carbon rich phases were prepared by exposing the Si rich phases at $1000\text{-}1050^\circ\text{C}$ to C_2H_2 . Carbon

clusters were formed on the surface after exposure of the (3×3) surface to 30 L of C_2H_2 at $1050^\circ C$ as shown in Fig. 3(a). Atomically resolved STM images showed local (2×2) ordering. At saturated coverage (100 L), one monolayer of Carbon was deposited on the surface (Fig. 3(b)), and the surface showed a (6×6) structure. Similar structures were observed on other Si rich phases.

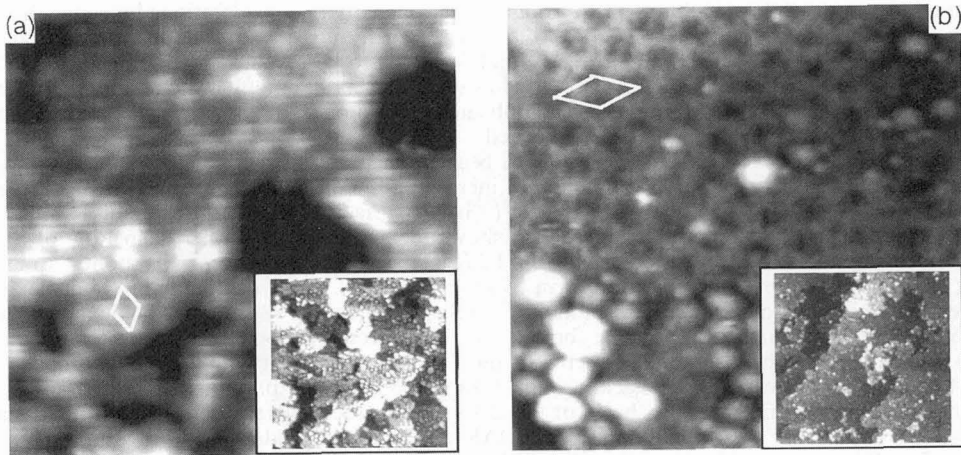


Figure 3: STM images of the C rich structure formed after interaction of the Si rich phases with C_2H_2 at $1050^\circ C$. (a) The (2×2) structure after 30 L of C_2H_2 exposure of (3×3) surface ($90\text{\AA} \times 90\text{\AA}$). The sample bias is $+2.0V$. The image size for the insert is $1200\text{\AA} \times 1200\text{\AA}$. (b) The empty-state image ($+1.6V$) of the (6×6) structure ($170\text{\AA} \times 170\text{\AA}$). The insert shows large scale image of the surface ($1200\text{\AA} \times 1200\text{\AA}$).

3.2 STRUCTURES OF THE C-TERMINATED SURFACE

Similar cleaning procedure was applied to the C-terminated surface. After expose the surface to Si flux at $950^\circ C$ for typically 5 min., the surface was clean and showed a $(2\sqrt{3} \times 2\sqrt{3})$ reconstruction. Large scan showed no well defined step structure, indicating that the surface was on-axis. Again height contrast reversal was observed with a honeycomb structure in the filled-state (Fig. 4(a)) and a hexagonal structure in the empty-state (Fig. 4(b)). Based on the same charge transferring mechanism, a Si-C alloy adatom model was proposed for this $(2\sqrt{3} \times 2\sqrt{3})$ reconstruction [13], as shown in Fig. 3(c). In the model, $1/3$ ML Si and C adatom bond to three surface C atom at the T_4 sites in an ordered $(\sqrt{3} \times \sqrt{3})$ array, but with the

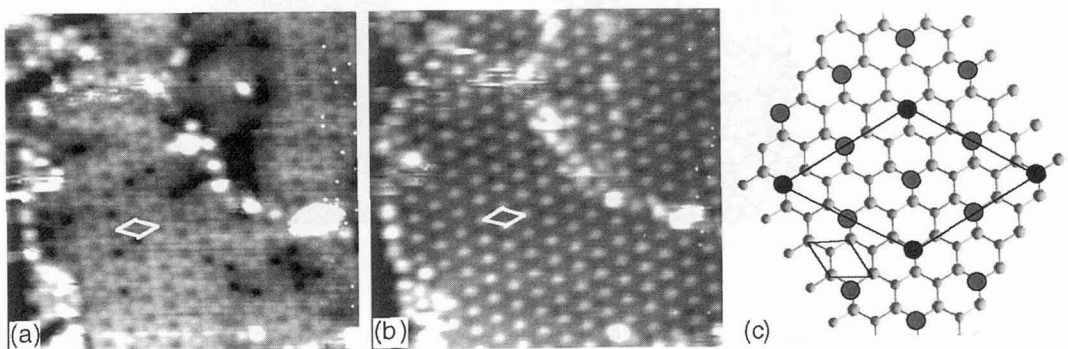


Figure 4: (a) Filled-state ($-1.6V$), and (b) empty-state ($+1.6V$) STM image of the $(2\sqrt{3} \times 2\sqrt{3})$ reconstruction ($150\text{\AA} \times 150\text{\AA}$). (c) Top view of the Si-C adatom alloy model. Large dark ball is the Si adatom, and shadowed ball is the C adatom. The adatoms locate at the T_4 sites.

chemical identity between Si and C varies in such a manner that the Si adatoms produce the $(2\sqrt{3}\times 2\sqrt{3})$ geometry, which give rises to the hexagonal array of protrusions revealed in the empty-state STM image, while the C adatoms form the honeycomb which was revealed in filled-state STM image. Again, the model is tentative, and cautious has to be taken in such a direct assignment of the features in STM image to the position of atoms.

The Si rich phases were also prepared by deposition of Si to the $(2\sqrt{3}\times 2\sqrt{3})$ surface as shown in Fig. 5. After about 1 ML of Si was deposited, the surface showed a local (2×2) ordering (Fig. 5(a)). Further deposition of Si on the (2×2) surface led to the formation of the (3×3) structure (Fig. 5(b)). Eventually, the

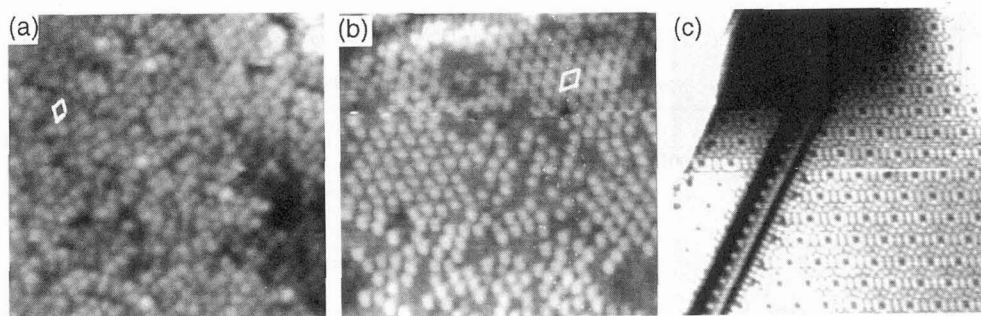


Figure 5: Sequence of STM images of the 6H-SiC $(000\bar{1})$ surface, showing the Si rich structures in the order of increasing Si concentration: (a) The (2×2) reconstruction ($160\text{\AA}\times 160\text{\AA}$); (b) The (3×3) reconstruction ($160\text{\AA}\times 160\text{\AA}$); (c) The coexisting of the (7×7) reconstruction and Si island ($300\text{\AA}\times 300\text{\AA}$).

DAS (7×7) structure was also formed after more Si was deposited on the (3×3) surface. Si islands were also observed. Shown in Fig. 5(c) is the STM image, indicating the coexisting of the (7×7) structure and a Si island. Atomically resolved images indicated that the Si islands were faceted into high-index (311) orientation of Si, which was (3×2) reconstructed.

Similarly, the interaction of C_2H_2 with the Si rich phases led to deposition of Carbon on the surface. Figure 6 shows the surface after exposing the (3×3) surface to 50 L of C_2H_2 at $1050\text{ }^\circ\text{C}$, which resulted in 1 ML of C coverage. Atomically resolved image showed that the surface was (1×1) reconstructed (Fig. 5(b)). The (1×1) structure is likely formed by a single layer of C bond to the top Si-C bilayer.

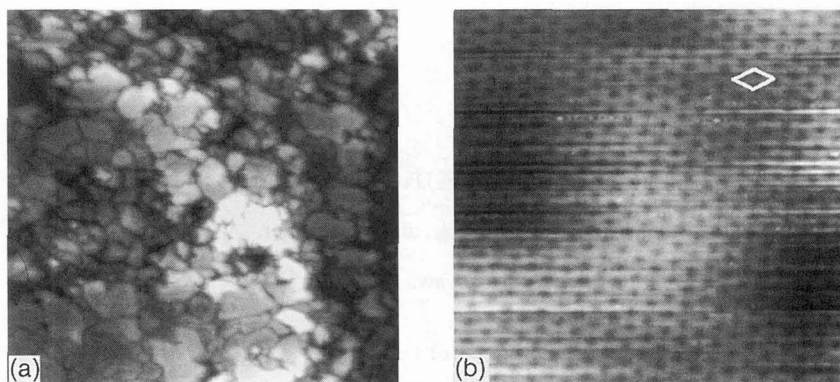


Figure 6: STM image of the (1×1) C rich surface after exposure the (3×3) surface to 50 L of C_2H_2 at $1050\text{ }^\circ\text{C}$. The image size is (a) $(1200\text{\AA}\times 1200\text{\AA})$, and (b) $(50\text{\AA}\times 50\text{\AA})$.

The phase diagram as a function of Si and C composition is shown in Fig. 7.

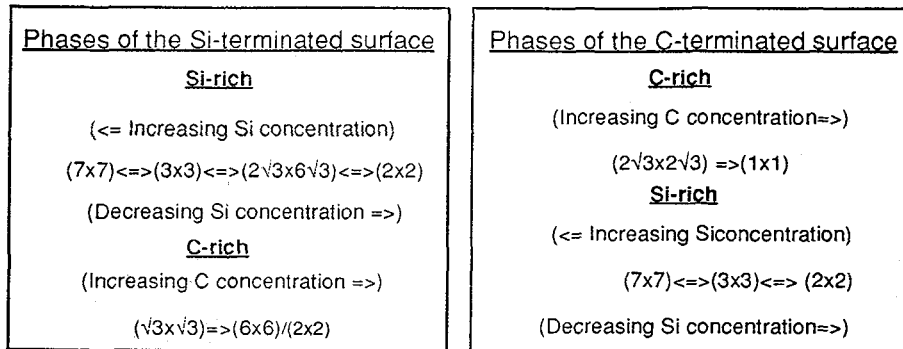


Figure 7: Phase diagram of the 6H-SiC (0001) and (000 $\bar{1}$) surface.

4. CONCLUSIONS

We have shown that in situ Si beam etching is very effective to remove the oxide of the 6H-SiC(0001) and (000 $\bar{1}$) surface. Moreover, the 6H-SiC surfaces exhibit a variety of reconstructions as summarized in Fig. 7, which may be used to regulate the growth process at an atomic level, as has been suggested [4]. Furthermore, since the reconstructed surface has fewer dangling bonds, and the symmetry of the reconstructed surface is different from the (1x1) surface, the growth energetics and kinetics are expected to be different. As in the case of the $(2\sqrt{3} \times 6\sqrt{3})$ surface (Fig. 2(b)), the rows will provide a easier diffusion path for adatoms compared with diffusion across the rows. Indeed, a study has shown that SiC films grown on the 6H-SiC(0001)-(3x3) substrate resulted in the step flow mode, and subsequently the films were 6H, while films grown on the (1x1) substrates resulted in two-dimensional nucleation and the SiC films were β -SiC [3].

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